Persistent dynamics in the $S = 1/2$ quasi-one-dimensional chain compound $\mathrm{Rb_4Cu(MoO_4)_3}$ probed with muon-spin relaxation

T. Lancaster,[1] P.J. Baker,[2] F.L. Pratt,[2] S.J. Blundell,[3] W. Hayes,[3] and D. Prabhakaran[3]

[1]*University of Durham, Centre for Materials Physics, South Road, Durham, DH1 3LE, UK*
[2]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, UK*
[3]*Oxford University Department of Physics, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, UK*
(Dated: February 25, 2013)

We report the results of muon-spin relaxation measurements on the low-dimensional antiferromagnet $\mathrm{Rb_4Cu(MoO_4)_3}$. No long-range magnetic order is observed down to 50 mK implying a ratio $T_N/J < 0.005$ (where J is the principal exchange strength along the spin chains) and an effective ratio of interchain to intrachain exchange of $|J_\perp/J| < 2 \times 10^{-3}$, making the material an excellent realization of a one-dimensional quantum Heisenberg antiferromagnet. We probe the persistent spin excitations at low temperatures and find that ballistic spin transport dominates the excitations detected below 0.3 K.

The one-dimensional $S = 1/2$ quantum Heisenberg antiferromagnet (1DQHAF) described by the Hamiltonian $H = J \sum \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1}$ continues to be of much interest, not only as a system in which quantum fluctuations control the low-temperature physical behavior[1], but also due to the question of whether the spin transport in this system is ballistic or diffusive[2,3]. However, the experimental verification of theoretical work relies on the existence of material systems whose interactions are well approximated by the assumptions of the model. Such systems include the inorganic compound[4,5] $\mathrm{Sr_2CuO_3}$, the organometallic coordination polymer[6] $\mathrm{Cu(pyz)(NO_3)_2}$ and the organic radical-ion salt[7] DEOCC-TCNQF$_4$.

Recently[8] the inorganic system $\mathrm{Rb_4Cu(MoO_4)_3}$ was identified as another candidate quasi-one-dimensional $S = 1/2$ magnetic system, where the principle magnetic exchange occurs along one-dimensional (1D) chains, with exchange strength J. Real systems do not comprise completely isolated chains and there are also interchain interactions described by an effective exchange coupling $J_\perp$. Such a coupling, although weak in comparison to J in many materials, controls the thermodynamics and leads to long-range magnetic order (LRO) at a nonzero temperature T_N. The ratio T_N/J is therefore a good indicator of the degree of isolation of a low-dimensional magnetic system. In fact, quantum Monte Carlo simulations of this effect provide a means of estimating the effective interchain coupling $J_\perp$ in a quasi-1D magnet via the expression[9]

$$|J_\perp| = \frac{T_N}{4c\sqrt{\ln\left(\frac{\lambda J}{T_N}\right) + \frac{1}{2}\ln\ln\left(\frac{\lambda J}{T_N}\right)}}, \qquad (1)$$

where $c = 0.233$ and $\lambda = 2.6$. It is important to note that the 1D nature of the spin system promotes strong thermal and quantum fluctuations which lower the magnitude of T_N, resulting in quite long-ranged correlations building up in the chains just above the ordering temperature, and also reduce the magnitude of the magnetic moment[12].
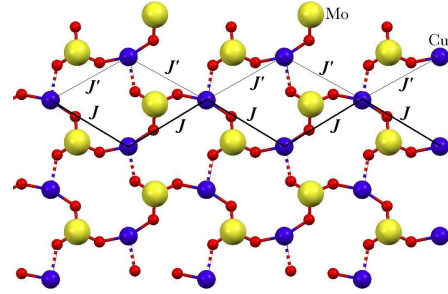

FIG. 1: The principal exchange paths in $\mathrm{Rb_4Cu(MoO_4)_3}$ (viewed along the b-axis) showing strong exchange (with strength J) and weak exchange (strength J') between $\mathrm{Cu^{2+}}$ ions through Cu-O-Mo-O-Cu paths. Weak exchange bonds between $\mathrm{Cu^{2+}}$ ions and apical oxygens are dotted.

These factors often make the identification of magnetic ordering difficult using thermodynamic probes. We have shown previously[6,10,11] that muons are often sensitive to LRO that can be very difficult to detect with conventional probes. At temperatures above T_N muon-spin relaxation (μ^+SR) may also be used to probe the nature of the spin excitations and their transport. In this paper we investigate the magnetism in $\mathrm{Rb_4Cu(MoO_4)_3}$ using implanted muons. We search for long range magnetic order down to 50 mK and investigate the spin excitations of the system. We argue that the system remains disordered at all measured temperatures and the persistent mode that dominates the dynamics we measure below 0.3 K is ballistic in character.

The structure[8] of $\mathrm{Rb_4Cu(MoO_4)_3}$ is layered, with triangular lattice sheets of $S = 1/2$ $\mathrm{Cu^{2+}}$ ions in the a-c plane [Fig. 1], separated by layers of $\mathrm{Rb^+}$ and $\mathrm{MoO_4}$. Although this constrains the principal exchange to occur along paths in the a-c plane, the two dominant exchange paths, with strengths J and J', are quite different. The strength of the exchange follows from the disposition of the $\mathrm{Cu^{2+}}$ $d_{x^2-y^2}$ orbitals[8]. The local environment of the
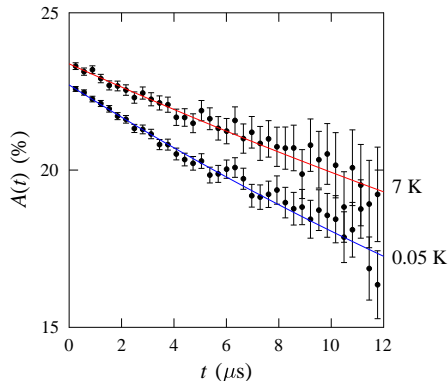
FIG. 2: Example ZF μ^+SR spectra measured at $T = 0.05$ K and $T = 7$ K.

copper is a CuO_5 distorted square pyramid which causes the $d_{x^2-y^2}$ orbitals to lie in the base of these pyramids. Strong σ bonds therefore link the $d_{x^2-y^2}$ orbitals on the Cu^{2+} and the $p_{x,y}$ orbitals on neighbouring O^{2-} ions that form the basal plane of the pyramids, with one strong O-Cu-O bond in the a-c plane and one directed along b. The main superexchange pathway, with strength J, therefore goes via two σ bonds in the a-c plane, along identical zig-zag Cu-O-Mo-O-Cu paths, as shown in Fig. 1. The other possible exchange path in this plane, which has strength J', is suppressed since it involves only one σ bond and also the O-Cu bond [shown with dotted lines in Fig. 1] that involves the apical oxygen of a CuO_5 unit, whose p_z orbitals enjoy very little overlap with the Cu^{2+} $d_{x^2-y^2}$ orbital. In this way, the spin system appears to be formed from one-dimensional chains with coupling J, with weak interchain coupling J' in the a-c plane and coupling between planes that is still weaker. This has led to the material being advanced as a strong candidate to show quasi-one-dimensional magnetic behavior. Magnetic susceptibility and heat capacity measurements[8] confirm that the dominant magnetic exchange occurs along strongly interacting antiferromagnetic chains with an exchange constant $J = 10.0$ K. No signature of LRO was detected down to 0.1 K, with only broad humps in susceptibility and heat capacity in the 4 K region, typical of the build up of short range correlations above T_N.

In a muon-spin relaxation (μ^+SR) experiment[13], spin-polarized positive muons are stopped in a target sample, where the muon usually occupies an interstitial position in the crystal. The observed property in the experiment is the time evolution of the muon spin polarization, the behavior of which depends on the local magnetic field B at the muon site, and which is proportional to the positron asymmetry function $A(t)$. Our μ^+SR measurements were made using the MuSR spectrometer at the ISIS facility, UK. For the measurement a polycrystalline sample of $Rb_4Cu(MoO_4)_3$ was mounted on a silver sam-

ple plate using a small amount of vacuum grease and the plate was attached to the cold finger of a dilution refrigerator.

Example zero-field (ZF) μ^+SR spectra are shown in Fig. 2. Across the entire measured temperature range ($0.05 \leq T \leq 50$ K) $A(t)$ is found to relax exponentially with small relaxation rates of $\lambda < 0.03$ MHz. Data were fitted to

$$A(t) = A_0 e^{-\lambda t} + A_{bg}, \qquad (2)$$

where A_{bg} is a small, constant offset reflecting the contribution of those muons that stop in the sample holder or cryostat tail. Oscillations, which would be characteristic of a quasi-static local magnetic field at the muon stopping site, are not observed at any temperature. However, we do observe a cross-over in magnetic behaviour in the system upon cooling below $T_{co} \approx 5$ K. Below this temperature the initial asymmetry drops by an amount $\Delta A = 0.7(1)\%$ (translating to a loss of roughly 3% of the total muon polarization) as shown in Fig. 3(b). Also evident is an increase in the relaxation rate λ, which begins to rise below 4 K, increases steadily and then flattens off below 0.3 K [Fig. (3(a)].

These results are indicative of a transition or cross-over below T_{co} to a regime characterized by larger magnetic fields, a broader distribution of fields or (perhaps most likely) an increased correlation time. Assuming the fast-fluctuation limit (justified below) we expect[14] the relaxation to vary as $\lambda \propto \Delta^2 \tau$, where Δ is proportional to the second moment of the field distribution via $\Delta^2 = \gamma_\mu^2 \langle B_\mu^2 \rangle$, γ_μ is the muon gyromagnetic ratio, B_μ is the magnetic field at the muon site and τ is the correlation time. The small fraction of asymmetry missing below T_{co} therefore reflects a fraction of muons which are quickly depolarized within the first ~ 0.1 μs and the increased relaxation of the remainder of the muons also indicates an increase in the magnitude or width of their field distribution via Δ or correlation time via τ. The small size of the muon relaxation rate (leading to a decay time that is rather slow in comparison to the length of our time window) means that reliably extracting a value of the asymmetry baseline is difficult. We do not, however, see any evidence for an increase in the apparent baseline on cooling through T_{co} as would be expected in a transition to static magnetism in a polycrystalline sample. (Such an increase occurs since 1/3 of muon spin components would be expected to lie along the direction of a static local field and then not be relaxed.) This suggests that the magnetic state is characterized by significant dynamics in the local field at the muon site(s) at all temperatures.

To understand the nature of the muon relaxation, measurements were made in applied magnetic field, directed parallel to the initial muon spin polarization. The application of fields of $B < 3$ mT leads to a repolarization of the asymmetry. In view of the form of the ZF spectra, fits were carried out to a dynamicized Kubo Toyabe (KT) function[14] with a field fluctuation rate $\nu = 1/\tau$. Fits to this function in applied field with a second moment of
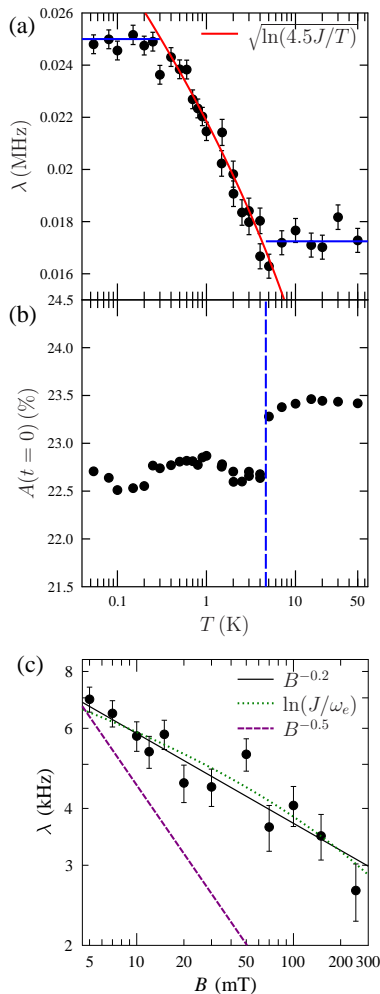
FIG. 3: (a) The relaxation rate λ as a function of temperature is seen to increase upon cooling through $T_{co} \approx 5$ K. (b) The initial asymmetry $A(t = 0)$ also shows a reduction upon cooling through T_{co} (dotted line). (c) The evolution of the relaxation rate λ with applied field (above $B = 3$ mT) at $T = 0.1$ K. All fits are described in the main text.

the field distribution $\Delta \approx 0.1$ MHz and a fluctuation rate $\nu \approx 0.7$ MHz describe the data at all measured fields below 5 mT. The ratio $\nu/\Delta \approx 7$ places the relaxation in the fast fluctuation limit, justifying the assumption above.

An obvious explanation for the change of behaviour around 5 K would be a transition to a state of LRO at T_{co}. Although one might expect that LRO would lead to oscillations in the asymmetry, there are several cases where such oscillations are not observed at a magnetic transition. Similarly the absence of an apparent increase in baseline does not preclude the occurrence of LRO either. However, we believe LRO unlikely. If $T_{co} = 4.8(3)$ K [which we estimate from the behavior of $A(t = 0)$] is identified with the magnetic ordering temperature T_N then we have a ratio $T_N/J = 0.48(3)$. The model in Eq. (1) refers

to a chain coupled weakly in the two perpendicular interchain directions, assumed identical, with strength $J_\perp$. Although the interchain coupling in $Rb_4Cu(MoO_4)_3$ is more complex, by applying Eq. (1) we obtain a prediction for an effective interchain coupling $|J_\perp| = 3.4(2)$ K which should be expected to be of the same order of magnitude as J' identified above. Using this estimate we find $|J_\perp/J| = 0.34(2)$, which would imply a rather three-dimensional magnetic material with little of the quite significant exchange anisotropy suggested by the structure or the previous magnetic measurements[8]. In addition, chain mean field theory gives us a predicted staggered moment[15] $m_0 = 1.017\sqrt{|J_\perp|/J} \approx 0.6\mu_B$, which is likely to be detectable. It therefore seems unlikely that the weak effects we observe with muons are LRO. Another possibility is that small phases of impurities are present and that these are ordering. In this picture the small loss of asymmetry would be due to the muons which stop in these regions and that the increased relaxation effect would reflect the magnetic field of the impurity regions in the rest of the sample. This seems highly unlikely in that if such impurities are detectable with μ^+SR their volume fraction must exceed several percent and their presence would likely have been detected with x-ray diffraction.

It is most probable that the effects we observe at T_{co} are due to the rapid growth of correlations in $Rb_4Cu(MoO_4)_3$ around 4 K. We note that broad peaks in magnetic susceptibility and in specific heat are both observed in the 4 K region[8]. These are due to the build up of magnetic correlations within the chains and reflects the fact that the energetic cost of flipping a spin is of order J. This build up could conceivably lead to local regions of well correlated spins which give rise to an increased muon relaxation. If that is the case then we must conclude that no LRO is observed down to 50 mK, placing strong constraints on the effective interchain coupling and the size of the staggered moment. We find $T_N/J < 0.005$, $|J_\perp| < 0.02$, $|J_\perp/J| < 2 \times 10^{-3}$ and $m_0 < 0.05\mu_B$. For comparison, we note that $Cu(pyz)(NO_3)_2$ has $|J_\perp/J| = 4.4 \times 10^{-3}$, Sr_2CuO_3 has $|J_\perp/J| = 0.93 \times 10^{-3}$ while DEOCC-TCNQF$_4$ has $|J_\perp/J| < 0.06 \times 10^{-3}$. These observations imply that $Rb_4Cu(MoO_4)_3$ is a better example of a 1DQHAF than $Cu(pyz)(NO_3)_2$ and perhaps comparable to Sr_2CuO_3.

That the physics of $Rb_4Cu(MoO_4)_3$ is well described by a 1D model of spin exchange with small interchain interactions allows us to relate our results to the spin excitations expected for such a model. Below T_{co} [Fig 3(a)] λ increases as the temperature is reduced, and saturates at a constant value $\lambda_{sat} = 0.025$ MHz below 0.3 K. This trend of an increased relaxation rate and low-T persistent dynamics is often seen in the μ^+SR of complex systems with low-temperature dynamics[16,17] but its origin is not fully understood. The general behavior can arise because of the existence of two relaxation channels, one of which is strongly T dependent with a correlation time $\tau_s(T)$ while the other shows little variation with T and has a correlation time τ_w. In the presence of two compet-

ing relaxation processes the one with the shorter correlation time wins out, giving the smaller relaxation rate. At higher temperature, therefore, we have $\tau_s(T) \ll \tau_w$ which results in a strongly T-dependent relaxation. We may gain an insight into the temperature dependent part of λ by by appealing to the results of previous measurements on highly ideal 1DQHAFs. The muon is a local probe, so its response is due to a sum over fluctuations at all wavevector q. However, NMR[18] of Sr_2CuO_3 and μ^+SR[7] of DEOCC-TCNQF$_4$ revealed that the low temperature relaxation was dominated by spinon excitations close to $q = \pi/a$ where low T corrections to the theory of spin correlations for the $S = 1/2$ 1DQHAF result in a rise in λ that follows $\lambda \sim \sqrt{\ln(4.5J/T)}$. Such a temperature dependence provides a good description of the rapid increase in λ at low temperatures in $Rb_4Cu(MoO_4)_3$ as shown in Fig. 3(a)[19]. The increase in relaxation rate arises from the lengthening of the correlation time τ_s with decreasing temperature. This increase continues until τ_s becomes much longer than the correlation time τ_w of the T-independent relaxation channel with persistent dynamics, which then dominates the relaxation at the lowest temperatures, resulting in a relaxation rate λ_{sat}.

Finally we turn to the nature of the propagation of the persistent spin fluctuation in $Rb_4Cu(MoO_4)_3$. Whether the excitations in 1DQHAFs are ballistic or diffusive remains a key question in the physics of spin chains and one that can be addressed with our LF μ^+SR measurements[7]. This is because the spectral density for ballistic motion is expected to vary with frequency ω as $f(\omega) \sim \ln(J/\omega)$ while 1D diffusive transport results in a function $f(\omega) \sim \omega^{-\frac{1}{2}}$. In applied fields $B > 3$ mT at $T = 0.1$ K we begin to repolarize the missing fraction of asymmetry

and obtain a relaxation that persists up to the highest applied field of 250 mT. The result of fitting this persistent relaxation rate to an exponential relaxation function as a function of applied field is shown in Fig. 3(c). We see that the diffusive model, with $\lambda \propto B^{-0.5}$ provides a poor description of the data. In fact, fitting to an unconstrained power law form $\lambda \propto B^n$ results in $n = 0.20(2)$, well below the theoretical value of $n = 0.5$ and the slightly reduced value of $n = 0.35$ found[7] in DEOCC-TCNQF$_4$. Turning now to the model of ballistic transport, we note that the muon can couple to electronic spin density via both dipolar and hyperfine interactions, and for ballistic spin transport we expect[20] a relaxation rate $\lambda(B) = \frac{1}{20}\left[3D^2 f(\omega_\mu) + (5A^2 + 7D^2)f(\omega_e)\right]$, where $\omega_\mu = \gamma_\mu B$, $\omega_e = \gamma_e B$, γ_e is the electron gyromagnetic ratio and A and D are the scalar and dipolar hyperfine coupling parameters. As shown in Fig. 3(c), a good fit to the data is achieved by fitting $\lambda \propto \ln(J/\omega_e)$, which assumes that the second term in the expression for $\lambda(B)$ dominates. Our inference, therefore, is that the modes which cause the saturated relaxation at low temperature show behavior suggestive of ballistic spin transport.

In conclusion, our results demonstrate that $Rb_4Cu(MoO_4)_3$ is a good example of a quasi-1DQHAF system, with a low ratio of exchange strengths $|J_\perp/J|$, putting it amongst the best realizations of this model. The spin excitations are suggestive of a contribution from modes around $q = \pi/a$ in the region $0.3 \leq T \leq 4$ K and a persistent, low temperature contribution which has a ballistic character.

[1] T. Giamarchi, *Quantum Physics in one dimension* (Oxford University Press, Oxford, 2004).

[2] J. Sirker, R.G. Pereira and I Affleck, Phys. Rev. Lett **103**, 216602 (2009).

[3] R. Steinigeweg and W. Brenig, Phys. Rev. Lett. **107**, 250602 (2011).

[4] A. Keren, L. P. Le, G. M. Luke, B. J. Sternlieb, W. D. Wu, and Y. J. Uemura , S. Tajima and S. Uchida, Phys. Rev. B **48**, 12926 (1993).

[5] N Motoyama, H Eisaki and S. Uchida, Phys. Rev. Lett. **76**, 3212 (1996).

[6] T. Lancaster, S.J. Blundell, M.L. Brooks, P.J. Baker, F.L. Pratt, J.L. Manson, C.P. Landee and C. Baines, Phys. Rev. B, **73**, 020410(R) (2006).

[7] F.L. Pratt, S.J. Blundell, T. Lancaster, C. Baines, S. Takagi Phys. Rev. Lett. **96**, 247203 (2006).

[8] R. Ishii, D. Gautreaux, K. Onuma, Y. Machida, Y Maeno, S. Nakatsuji, J.Y. Chan, J. Am. Chem. Soc., **132**, 7055 (2010).

[9] C. Yasuda, S. Todo, K. Hukushima, F. Alet, M. Keller, M. Troyer and H. Takayama, Phys. Rev. Lett **94**, 217201 (2005).

[10] T. Lancaster *et al.*, Phys. Rev. B **75**, 094421 (2007).

[11] S.J. Blundell, T. Lancaster, F. L. Pratt, P. J. Baker, M. L. Brooks, C. Baines, J. L. Manson and C. P. Landee, J. Phys. Chem. Solids **68**, 2039 (2008).

[12] P. Sengupta, A. W. Sandvik, and R. R. P. Singh, Phys. Rev. B **68**, 094423 (2003).

[13] S.J. Blundell, Contemp. Phys. **40**, 175 (1999).

[14] R.S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki and R. Kubo, Phys. Rev. B **20**, 850 (1979).

[15] H. J. Schulz, Phys Rev. Lett. **77**, 2790 (1996).

[16] T. Lancaster, S.J. Blundell, F.L. Pratt, I. Franke, A.J. Steele, P.J. Baker, Z. Salman, C. Baines, I. Watanabe, S. Carretta, G.A. Timco and R.E.P. Winpenny, Phys. Rev. B **81**, 140409(R) (2010).

[17] J.S. Gardner, M.J.P. Gingras and J.E. Greedan, Rev. Mod. Phys. **82**, 53 (2010).

[18] M. Takigawa, O.A. Starykh, A. W. Sandvik and R.R.P. Singh, Phys. Rev. B **56** 13681 (1997).

[19] Fitting this functional form to the data yields an estimate of the exchange constant which is consistent with the $J = 10.0$ K derived from magnetic susceptibility.

[20] F. Devreaux, J.P. Boucher and M. Nechtshein, J. Phys. **35**, 271 (1974).